

CO/H₂ AND CO₂/H₂ REACTIONS WITH AMORPHOUS CARBON-METAL CATALYSTS

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By metal impregnation of selected naturally occurring organic materials followed by controlled carbonization, metal semicoke catalysts can be readily prepared. These catalysts have been tested in the synthesis of hydrocarbons and alcohols from CO/H₂ and CO₂/H₂ mixtures. Fe and Co preparations have been used. Relatively high temperatures are required when using these catalysts, which are quite active for synthesis using CO₂ and H₂. The pressure (5150 kPa) is very favorable both for the synthesis of liquid hydrocarbons (C₅-C₃₀) and alcohols (C₁-C₅).

Металлической пропиткой избранных природных органических материалов с последующей контролируемой карбонизацией могут быть приготовлены металлические полукоксовые катализаторы. Эти катализаторы были использованы в синтезе углеводородов и спиртов из смесей CO/H₂ и CO₂/H₂. Были использованы Fe и Co. Относительно высокие температуры необходимы при применении этих катализаторов, являющихся весьма активными в синтезе из CO₂ и H₂. Давление 5150 кПа) весьма благоприятно при синтезе жидких углеводородов (C₅-C₃₀) и спиртов (C₁-C₅).

INTRODUCTION

The catalytic synthesis of hydrocarbons and alcohols from mixtures of CO/H₂ is being studied with renewed interest. A number of studies /1-3/ have shown the importance of the nature of the metal as well as that of the support since they influence both the reactivity and the selectivity of the reaction. Carbon supports, in a variety of forms, have recently been the subject of intense work /4-5/.

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The present work shows new results on the activity and selectivity of amorphous carbon-metal catalysts (semi-coke from peat and metal either Fe or Co) for the catalytic synthesis of hydrocarbons and alcohols from CO/H₂ and also from CO₂/H₂. Until recently, studies on synthesis from this last mixture have been somewhat neglected, and the renewed interest /6–10/ is obviously related to the significant potential of CO₂ in the field of energy.

In an earlier study /11/ we described the systematic preparation procedure as well as the influence of space velocity, temperature and the aging of the amorphous carbon-metal catalyst (M = Ni) in atmospheric pressure synthesis conditions. Our new work shows the possibilities of more extensive syntheses (gaseous and liquid hydrocarbons, alcohols) from Fe or Co-amorphous carbon catalysts with CO/H₂ and CO₂/H₂ mixtures at atmospheric or higher pressures (5150 kPa).

EXPERIMENTAL

The amorphous carbon-metal catalysts are obtained simply and cheaply by impregnation of an appropriate organic compound (peat) followed by controlled pyrolysis. The preparation procedure has been well documented in previous papers /4, 12/.

The carbonization yield is in the region of 40% for all the examples. Catalysts used in the present study are: Fe-amorphous carbon (BET 364 m²/g, 0.120 g metal/g catalyst), Co-amorphous carbon (BET 212 m²/g, 0.128 g metal/g catalyst).

X-ray analysis allowed the determination of the state of the metal on the amorphous carbon matrix. Cobalt is present in metallic form, iron also in metallic form and as oxides (Fe₃O₄ and Fe₂O₃) as well.

The catalytic synthesis of hydrocarbons and alcohols

Methods

The experiments were carried out in an apparatus consisting of a stainless steel reactor (length 400 mm, internal diameter 8 mm), electrically heated, and preceded by a preheating system (length 200 mm). The liquids formed are retained in a high pressure trap, cooled by water and the gases are expanded at the exit (300 kPa for the experiments at 5150 kPa). (Low Pressure Cylinder Air Liquid D. E. 38, regulator Air Liquid 421, controller Setaram U 70). One of the characteristics of the reactor is that it can be used with a powdered catalyst. This is placed in an internal tube in the reactor (outer diameter 7.8 mm) between two plugs of glass-wool.

Reaction conditions

The preparation of the catalyst is carried out in situ. The reactor is first flushed thoroughly with H₂ (0.5 h, 100 ml/min then heated, in steps, up to 400 °C (1/2 h to 120 °C, 1/2 h to 260 °C, 40 h to 400 °C). The temperature of the reactor is then adjusted to the temperature of the reaction (375 °C) and the reaction mixture is introduced onto the catalyst. The first gas samples are taken after one hour, T = 375 °C, P = 103 or 5150 kPa, CO/H₂ 1/1, CO₂/H₂ 1/4, GSV: 20 l h⁻¹g⁻¹ catalyst.

Chromatography conditions*

The analysis of CO, CO₂, H₂, gaseous hydrocarbons and alcohols has been described in an earlier work /13/. Analysis of the hydrocarbons C₅ to C₃₀ is carried out using the following conditions: Apparatus GIRDEL 3000 FID, polymethylsiloxane column 35 m, diameter 0.3 mm, temperature: by steps to 50 °C, 7 min then programming from 50 °C to 270 °C, 4 °C/min. Gas vector: N₂, 2 ml/min; T injector: 250 °C; T detector: 300 °C.

RESULTS AND DISCUSSION

Reaction with CO/H₂

The pressure has an important influence on the activity, the rate of consumption of CO is multiplied by 9.5 for iron and 15.9 for cobalt, when the pressure is varied from 103 kPa to 5250 kPa. The distribution of the products obtained is even more drastically affected: only gaseous hydrocarbons and CO₂ at 103 kPa, whereas gaseous hydrocarbons (82.9 and 96%), liquids (9.9 and 0.3%) and alcohols (7.2 and 3.7%) at 5150 kPa (for the iron and cobalt respectively) as shown in Table 1.

– Gaseous hydrocarbons: the distribution of the gaseous products is appreciably altered by pressure: for the iron there was an important reduction of CH₄ (41.5 to 18.5%) which increased the fractions C₃ to C₄ and above all decreased the yield of C₂ olefins/ΣC₂ formed with an increase in pressure (103 to 5150 kPa). This phenomenon has also been noticed by Kikuchi /14/. For cobalt, the variations are less marked but show the same trends.

– Liquid hydrocarbons: the analysis of the liquid hydrocarbon fractions (C₅ to C₃₀) (catalyst Fe) shows the presence of saturated hydrocarbons (53%), α-olefins

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Table 1
 Reactivity of Fe or Co peat-semi-coke with 1 : 1 CO/H₂
 (T = 375 °C, GSV = 20 l h⁻¹ g⁻¹ catalyst)

P (kPa)	103	5150	103	5150
Catalyst	12.0% Fe	12.0% Fe	12.8% Co	12.8% Co
Rate of CO consumption (mol g ⁻¹ metal sec ⁻¹ x 10 ⁻⁶)	7.4	70.4	10.2	162.2
Product composition (gas)				
CH ₄	41.5	18.3	58.7	52.8
CO ₂	34.7	44.2	24.5	23.9
C ₂ ^{''}	17.7	5.0	8.1	0.5
C ₂	1.5	7.8	5.6	7.8
C ₃ ^{''}	4.6	9.6	3.1	3.4
C ₃	—	3.6	—	4.7
C ₄	—	6.5	—	3.2
C ₅	—	5.0	—	—
Product composition (alcohols)				
MeOH	—	31.7	—	36.5
EtOH	—	43.9	—	41.3
iPrOH	—	5.9	—	2.7
PrOH	—	14.6	—	13.3
BuOH	—	3.9	—	4.8
C ₅ OH	—	traces	—	1.6

(10%) and branched hydrocarbons and internal olefins (37%) (not separated by G. P. C.), with two maxima for the linear saturated hydrocarbons at C₈ (3.9%) and C₁₃ (4.6%) and for α -olefins C₉ (0.8%) and C₁₃ (1.3%). From C₁₃ the hydrocarbons decrease regularly up to C₃₀. With the cobalt catalyst, the maximum of the linear saturated hydrocarbons is found equally between C₈ and C₁₃, but the proportion of α -olefins falls with an increase of the linear saturated hydrocarbon as found in the literature /15/. The two maxima in the saturated hydrocarbon distribution curve have already been obtained by Blanchard /16/.

— Alcohols were obtained in the highest percentage in the case of iron. For iron as for cobalt, there is a predominance of ethanol over methanol.

The analysis of the gaseous fractions between 1 and 20 hours shows a continuing development towards heavier gaseous hydrocarbons (25.3% and 69.9% CH₄ for Fe and Co after 1 hour, 6.5 and 3.7% after 20 hours), (1.2% and 3.3% of C₄ after 1 hour, 6.5 and 3.7% after 20 hours for Co and Fe). The proportion of CO₂ varies only slightly.

Table 2
 Reactivity of the Fe or Co peat semi-coke catalyst with 1 : 4 CO₂/H₂
 (T = 375 °C, GSV = 20 l h⁻¹ g⁻¹ catalyst)

P (kPa)	Catalyst	Consumption of CO ₂ ⁻¹ (mol g ⁻¹ metal sec ⁻¹ × 10 ⁻⁶)	Composition of the gas (mol %)							Composition of alcohols (mol %)	
			CH ₄	CO	C ₂ '	C ₂	C ₃ '	C ₃	C ₄	MeOH	EtOH
103	12.0% Fe	140.6	15.2	81.0	—	2.8	—	0.8	0.2	—	—
5150	12.0% Fe	202.2	30.3	59.3	0.2	6.7	0.3	2.6	—	74.0	26.0
103	12.8% Co	135.9	92.2	7.8	—	—	—	—	—	—	—
5150	12.8% Co	282.0	83.4	16.3	—	0.3	—	—	—	—	—

Our results with iron and cobalt on amorphous carbon catalysts, although carried out under different experimental conditions can be compared favorably with the results obtained on a graphite support /14, 16, 18/.

Reactions with CO₂/H₂

These reactions seem to depend heavily on the nature of the metal for their reactivity: Ni (89.9 μmol g⁻¹ metal sec⁻¹) /11/ compared to 140.6 and 135.9 for Fe and Co. This activity is significantly greater than for CO/H₂ (22, 7.4, 10.2 on our catalysts Ni, Fe, and Co). Our results (Table 2) confirm those of Trambouze on Ni /6/ /10/, and Somorjai /7/ /19/ on iron.

The influence of pressure is less crucial than for CO/H₂. The consumption of CO₂ is only multiplied by 1.4 and 2.1 for Fe and Co on passing from 103 to 5150 kPa.

The selectivity is also very different depending on the metal used (80.7% CO, 19.2% CH₄; 81.0% CO, 15.2% CH₄; 7.8% CO and 92.2% CH₄; for Ni, Fe and Co respectively), at atmospheric pressure. With higher pressures for iron there is a net decrease in the proportion of CO with an increase of gaseous hydrocarbons (above all methane). The appearance of alcohols must also be noted (0.5% of CO₂ transformed); for cobalt, the proportion of CH₄, while remaining at a high level (83.4%), decreases with an increase of CO.

Generally, as is verified in the literature /19/, the mixture CO₂/H₂ limits the formation of hydrocarbons and alcohols in terms of C₁.

CONCLUSIONS

The amorphous carbon-metal catalysts can be made simply and easily. They function at an abnormally high reaction temperature (between 350 and 400 °C) with an activity comparable to those prepared on other supports. Significant chemisorption of CO, CO₂ and H₂ on the amorphous carbon catalyst could be the cause of the high activity and the high operating temperatures required. The mobility of the chemisorbed carbon oxides will begin to be important at the observed synthesis temperatures. These new catalysts are active for synthesis from CO₂ and H₂. This property could be of interest in the direct use of gases resulting, for example, from the gasification of coal and biomass products.

The use of pressure is advantageous with iron and cobalt catalysts, allowing synthesis to be directed towards liquid hydrocarbons and alcohols.

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